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Structural phase diagram and isomery in flexible honeycomb-like 2D hydrogen bonded solid solutions

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Solid solution of Hydrogen bonded networks of formula $((1-2H^+)_{3x}(2-2H^+)_{3(1-x)}([Fe(CN)_6]^{3-2})). nH_2O$, where $(1-2H^+)$ and $(2-2H^+)$ are bisamidinium H bond donor entities, have been synthesized and structurally analysed. The H bonded systems display a honeycomb-like structure, and depending on the x value, three different pavages of the (6,3) system are observed, leading to three different phases. The precise location of the H bond donor cations $(2-2H^+)$ have been performed, evidencing H bonding between adjacent cations. Thermal properties of the solid solutions have been performed.

Introduction

A crystalline solid solution is a mixture of at least two crystalline pure phases that coexist as a new crystalline phase. Kitaigorodsky¹, through his pioneering work, showed that in mixed crystals the relationship between composition and structure property is often described by Vegard's law.² When the components of the solid solution are molecular entities, these systems can be called molecular alloys.³ Engineering molecular crystals with multicomponents that form solid solution or molecular alloys is a hot topic in material science because of their new or superior functionalities such as optics,⁴ ferroelectric,⁵ catalysis⁶ or magnetism.⁷ In order to enhance the collective properties of such entities, structural property correlation is a crucial issue. The structure prediction including the recognition pattern between the molecular components, and the crystal packing in the crystal, is still an open topic.⁸ Substantial progress has been made recently in crystal structure prediction, however obtaining crystals with desired space group symmetry and controlled arrangement of supramolecular motifs still remains a great challenge.⁹

Through the *molecular tectonics*¹⁰ approach, the design and synthesis of supramolecular architectures was achieved.¹¹ We demonstrated the building of large families of components

held by hydrogen bonds and rationalised their recognition pattern, and thus the formed molecular networks.^{12, 13}

While the majority of reported molecular solid solutions are inorganic in nature,¹⁴ there are few examples of organic solid solutions in the crystalline state.¹⁵ For the formation of solid solution, hydrogen bonding¹⁶ but also charge-assisted H-bonding¹⁷ is one of the very important used strategies, due to their flexibility and reliability.¹⁸

The co-crystallization of polymorphic hydrogen bonded networks is a unique opportunity to explore the different connectivity patterns that a molecular system may adopt. The influence of the connectivity pattern on the collective properties of a network is also an interesting illustration of the structure-property correlations. In the field of mixed crystals, it has been shown how non-stoichiometric mixtures can afford precise tuning of the optical properties, for example.¹⁹ Concerning hydrogen bonded systems, the solid solution maybe a tool for controlling lattice metrics, magnetic properties, absorption spectrum, polymorphism, and sorption properties.²⁰ In the case of hydrogen bonded systems, we have also shown that the porosity may be tuned by controlling the ratio of cations in solid solutions.^{13d}

In this context, we have investigated different possible connectivity patterns in a series of solid solutions of H bonded systems, presenting different crystallographic phases. The solid solutions are based on the mixture of organic ligand that will lead to distinct crystallographic phases.

We have already shown that bisamidinium dications $(1-2H^+)$ and $(2-2H^+)$ (Figure 1) have been well designed as H-bond donors, and when combined with carboxylates or cyanometallates it leads to 1D or 2D charge-assisted networks (fig. 1).¹² For example, their associations with octahedral $[M(CN)_6]^{3-}$ ($M = Fe, Co$ or Cr) cyanometallates leads to porous

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H bonded isostructural crystals with a 2D dimensionality.^{12,13a,b,21}

More precisely, when bisamidinium dications ($1\text{-}2\text{H}^+$) and ($2\text{-}2\text{H}^+$) (figure 1, top) are combined with $[\text{M}(\text{CN})_6]^{3-}$, 2D honeycomb-like networks ((6,3) networks) result, presenting the same connectivity pattern between anions and cations. ($1\text{-}2\text{H}^+$)₃[[Cr(CN)₆]³⁻]₂ and ($2\text{-}2\text{H}^+$)₃[[M(CN)₆]³⁻]₂ (M = Fe, Co, and Cr), crystallise in the $P2_1/n$ space group, whereas ($1\text{-}2\text{H}^+$)₃[[Fe(CN)₆]³⁻]₂ and ($1\text{-}2\text{H}^+$)₃[[Co(CN)₆]³⁻]₂ crystallise in the $P\bar{1}$ space group.^{13a,b,21} As shown by their crystallographic parameters presented in table 1, ($1\text{-}2\text{H}^+$)₃[[Fe(CN)₆]³⁻]₂ · 7H₂O (compound **3**) and ($2\text{-}2\text{H}^+$)₃[[Fe(CN)₆]³⁻]₂ · 8H₂O (compound **9**) are not isostructural.

Table 1: Crystallographic data for ($1\text{-}2\text{H}^+$)₃[[Fe(CN)₆]³⁻]₂ (**3**) and ($2\text{-}2\text{H}^+$)₃[[Fe(CN)₆]³⁻]₂ (**9**) recorded at 173K.²¹

	($1\text{-}2\text{H}^+$) ₃ [[Fe(CN) ₆] ³⁻] ₂ · 7H ₂ O (3)	($2\text{-}2\text{H}^+$) ₃ [[Fe(CN) ₆] ³⁻] ₂ · 8H ₂ O (9)
Space Group	$P\bar{1}$ Phase A	$P2_1/n$ Phase C
a (Å)	7.0949(3)	7.0978(5)
b (Å)	12.3765(5)	22.2254(16)
c (Å)	17.9534(7)	20.6357(12)
α (°)	83.580(2)	90
β (°)	87.6101(10)	92.363(3)
γ (°)	83.9340(10)	90
V (Å ³)	1557.12(11)	3252.5(4)

Concerning the crystallographic parameters, compounds **3** and **9** display quite different cell parameters and a similar recognition pattern between anions and cations (leading to a (6,3) network). The recognition of $[\text{Fe}(\text{CN})_6]^{3-}$ with ($X\text{-}2\text{H}^+$), with a 2/3 stoichiometry, leads to distorted hexagons, through the connections of anionic ($[\text{Fe}(\text{CN})_6]^{3-}$ / ($X\text{-}2\text{H}^+$)) 1D arrays by ($X\text{-}2\text{H}^+$) cations. In the case of ($2\text{-}2\text{H}^+$), a shift of the connecting bisamidinium cations ($2\text{-}2\text{H}^+$) between the 1D anionic arrays is observed, enabling the switching of crystallographic space groups from $P\bar{1}$ ($1\text{-}2\text{H}^+$, **3**) to $P2_1/n$ ($2\text{-}2\text{H}^+$, **9**), as shown in figure 1.²¹ The driving force of this feature is the HO...OH interactions, of two hydroxyl groups belonging to two adjacent ($2\text{-}2\text{H}^+$) cations located on each side of the $[\text{Fe}(\text{CN})_6]^{3-}$ anions, with O-O distance of 2.828(5) Å, in compound **9**, whereas this interaction is of course not observed in compound **3**. In addition, other types of H-bonds, such as O₂H...N≡C, O₂H...OH, H₂O...HO-C, H₂O...H₂O, further stabilize this disposition, as shown in figure 1.²¹

Figure 1: Schematic recognition pattern of 2D (6,3) H bonded networks formed by combination of dications ($1\text{-}2\text{H}^+$) (compound **3**) and ($2\text{-}2\text{H}^+$) (compound **9**) with $[\text{Fe}(\text{CN})_6]^{3-}$.²¹

Through this study we intend to explore the potential recognition pattern in these two components systems ($[\text{Fe}(\text{CN})_6]^{3-}$ and $Y\text{-}2\text{H}^+$ ($Y=1$ or 2)) by investigating the solid state solutions formed by mixing the organic ligand leading to 2D H bonded solid solutions of formula ($1\text{-}2\text{H}^+$)_{3x}($2\text{-}2\text{H}^+$)_{3(1-x)}}[[Fe(CN)₆]³⁻]₂ · n H₂O, compounds **3-9**, ($0 < x < 1$). Their related thermal properties will also be discussed.

Results and discussion

Preliminary study

There are two main issues when analysing the structures of the resulting solid solutions of formula ($1\text{-}2\text{H}^+$)_{3x}($2\text{-}2\text{H}^+$)_{3(1-x)}}[[Fe(CN)₆]³⁻]₂ · n H₂O. The recognition pattern between anions and cations is based on the principle of a deformed and flexible honeycomb-like structure, held by hydrogen bonds.

- 1) The first issue is linked with the deformation of the hexagons in the honeycomb-like structure, induced by a shift of the ($2\text{-}2\text{H}^+$) cations, due to short O-H...OH interactions, as shown in figure 1. It is thus related to the pavage adopted by the resulting (6,3) network.
- 2) The second issue is the precise location of both organic cations ($1\text{-}2\text{H}^+$) and ($2\text{-}2\text{H}^+$) in the network formed by the solid solutions, since they may be crystallographically distinguished.

We performed a preliminary model analysis to explore the potential localisation of the cations ($1\text{-}2\text{H}^+$) and ($2\text{-}2\text{H}^+$) in the

solid solutions of formula $(1\text{-}2\text{H}^+)_{3x}(2\text{-}2\text{H}^+)_{3(1-x)}[\text{Fe}(\text{CN})_6]^{3-}_2 \cdot n\text{H}_2\text{O}$. There are four (five) peculiar x values to be analysed: $x=1/6$ (or $x=5/6$) ($1(1\text{-}2\text{H}^+)$ and $5(2\text{-}2\text{H}^+)$ in a 6-membered rings), $x=1/3$, $x=1/2$, $x=2/3$.

The representation of the different isomeric patterns with higher symmetry (other lower symmetries are not depicted here) is displayed in figure 2, together with the corresponding unit cell. One can note that for the x value = $1/2$, two different isomeric 2D H bonded networks, with different unit cells, are determined (figure 2c and 2d).

In this context, we can see that the precise location of the organic cations ($1\text{-}2\text{H}^+$) and ($2\text{-}2\text{H}^+$) can highly influence the unit cell, and the space group in which the H-bonded system may crystallise.

Figure 2: Six possible high symmetry arrangements in the $(1\text{-}2\text{H}^+)_{3x}(2\text{-}2\text{H}^+)_{3(1-x)}[\text{Fe}(\text{CN})_6]^{3-}_2$ solid solutions with the following composition for x : $x=5/6$ (a), $x=4/6$ (b), $x=3/6$ (c), $x=3/6$ (d), $x=2/6$ (e) or $x=1/6$ (f).

Description and discussion of the obtained solid-state solutions

Single crystals of mixtures of bisamidinium dications ($1\text{-}2\text{H}^+$) and ($2\text{-}2\text{H}^+$) combined with hexacyanoferrate(III), have been synthesized by solvent diffusion method in water solutions (see experimental part and also ref. 21). For the synthesis of solid solution with formula $(1\text{-}2\text{H}^+)_{3x}(2\text{-}2\text{H}^+)_{3(1-x)}$

$[\text{Fe}(\text{CN})_6]^{3-}_2 \cdot n\text{H}_2\text{O}$, we used the $(1\text{-}2\text{H}^+)/ (2\text{-}2\text{H}^+)$ ratios for the modelling study of isomeric solid solutions: $x=5/6$, $x=2/3$, $x=1/2$, $x=1/3$ or $x=1/6$ (figure 2), leading to crystalline compounds **4-8** respectively. All the obtained crystals have been analysed by X ray diffraction on single crystals and the observed ratios were refined and slightly different from the starting ratios, as seen in table 2: this behaviour was already documented for other molecular self-assembled systems.²² It is also important to note that for compounds **4-8** (solid solutions), relative oxygen occupancies of the hydroxyl group in ($2\text{-}2\text{H}^+$), were refined around each ($2\text{-}2\text{H}^+$) cationic units and the refined occupation rate values are reported in table 2.

Table 2: Data for the $(1\text{-}2\text{H}^+)_{3x}(2\text{-}2\text{H}^+)_{3(1-x)}[\text{Fe}(\text{CN})_6]^{3-}_2 \cdot n\text{H}_2\text{O}$ solid solutions (compounds **3-9**): observed phases, isomeric patterns and refined occupation rates for O in cation ($2\text{-}2\text{H}^+$)

	x	Phase	Isomeric pattern	Refined occupation rate of O in cation ($2\text{-}2\text{H}^+$)
$[1\text{-}2\text{H}^+]_3[\text{Fe}(\text{CN})_6]^{3-}_2 \cdot 7\text{H}_2\text{O}$ 3 ²¹	1	A $P\bar{1}$	-	-
$([1\text{-}2\text{H}^+]_{0.80}[(2\text{-}2\text{H}^+)_{0.20}]_3[\text{Fe}(\text{CN})_6]^{3-}_2 \cdot 7\text{H}_2\text{O}$ 4	0.80	A $P\bar{1}$	1/3 fig. 2e	0.3 and 0.3
$([1\text{-}2\text{H}^+]_{0.67}[(2\text{-}2\text{H}^+)_{0.33}]_3[\text{Fe}(\text{CN})_6]^{3-}_2 \cdot 8\text{H}_2\text{O}$ 5	0.67	B $P2_1/n$	1/3 fig. 2e	0.5 and 0.5
$([1\text{-}2\text{H}^+]_{0.53}[(2\text{-}2\text{H}^+)_{0.47}]_3[\text{Fe}(\text{CN})_6]^{3-}_2 \cdot 8\text{H}_2\text{O}$ 6	0.53	B $P2_1/n$	1/3 fig. 2e	0.7 and 0.7
$([1\text{-}2\text{H}^+]_{0.37}[(2\text{-}2\text{H}^+)_{0.63}]_3[\text{Fe}(\text{CN})_6]^{3-}_2 \cdot 8\text{H}_2\text{O}$ 7	0.37	B $P2_1/n$	-	0.8, 0.8 and 0.3
$([1\text{-}2\text{H}^+]_{0.17}[(2\text{-}2\text{H}^+)_{0.83}]_3[\text{Fe}(\text{CN})_6]^{3-}_2 \cdot 8\text{H}_2\text{O}$ 8	0.17	C $P2_1/n$	-	0.8, 0.8 and 0.9
$[2\text{-}2\text{H}^+]_3[\text{Fe}(\text{CN})_6]^{3-}_2 \cdot 8\text{H}_2\text{O}$ 9 ²¹	0	C $P2_1/n$	-	1

Crystallographic data for **4-8** are summarized in the crystallographic Table 3. For **4-8**, the bond and angles in the solid solutions are not discussed here since these values are close to the reported values for **3** and **9**.²¹ The location of the water molecules present in the lattice will also not be discussed. Compounds **5-8** present 8 water molecules in the unit cell, whereas compound **4** presents only 7 water molecules in the unit cell (see table 2).

Observed pavages of the (6,3) network

Compound **4-8** present all the same recognition pattern between anions and cations, but differ by the pavage adopted by the (6,3) network.

Compound **4**, presenting a x value $x = 0.80$, crystallizes in the triclinic $P\bar{1}$ space group and is isostructural (isomorphous and isometric) with **3** (Phase **A**).^{12,13a,b,21} It is important to note that in both compounds **3** and **4**, the same number of water molecules was found: 7.

Compound **8**, presenting a x value $x = 0.17$, crystallizes in the monoclinic $P2_1/n$ space group and is isostructural (isomorphous and isometric) with **9** (Phase **C**), and **8** and **9** present the same number of water molecules in the lattice: 8;

For compounds **5-7**, presenting a x value $0.80 > x > 0.17$, a new crystallographic phase has been evidenced, with monoclinic $P2_1/n$ space group (Phase **B**), but with different cell parameters (metrics) compared to the one of phase **C** (see tables 2 and 3).

The obtained solid solutions (compounds **4-8**) crystallizes reproducibly in three different phases: **A**, **B** and **C**.

These crystallographic phases **A**, **B** and **C** display here different pavages of the deformed honeycomb-like structure, as schematically presented in figure 3. They result from the metric constraints imposed by the use of $[\text{Fe}(\text{CN})_6]^{3-}$ and also from the recognition between $(2\text{-}2\text{H}^+)$ cations, through specific H bonds. The obtained 2D patterns (pavage) are topologically equivalent, but different from a metric point of view. They correspond to the *pmg2*, *pgg2* and *pg* Wallpaper groups for phases **A**, **B** and **C** respectively.²³

Figure 3: Schematic representations of the recognition patterns for the three types of deformed honeycomb-like 2D networks obtained for Phase **A** (a), Phase **B** (b) and Phase **C** (c). Yellow circles represent the metal centres.

Localization of the $(x\text{-}2\text{H}^+)$ cations in the unit cell

For **4-8**, concerning the location of the cations $(1\text{-}2\text{H}^+)$ and $(2\text{-}2\text{H}^+)$ in the networks, only one isomer (figure 2e, modelling, $x=1/3$) is observed, among the 6 that were displayed in modelling. For **4-8**, the precise x value is then reached by a different occupancy rate for the oxygen atom in $(2\text{-}2\text{H}^+)$, as shown in table 2.

Surprisingly, we found that for compounds **4-6** (x varying between 0.80 and 0.53, figure 4a or b), the location of the observed $(1\text{-}2\text{H}^+)$ and $(2\text{-}2\text{H}^+)$ cations within the network corresponds to the pattern described for the value $x=1/3$ (figure 2e), independently on the observed pavage (phase **A** or phase **B**).

For **7** and **8** (x values below 0.53, phase **B** or phase **C**, figures 4 c and d), $(2\text{-}2\text{H}^+)$ cations are occupying all the possible locations with increasing occupancies rates, and no positional isomer is observed.

This isomer ($x=1/3$, figure 2e), is mainly favoured by the interactions, through H bonds, of two hydroxyl groups belonging to adjacent $(2\text{-}2\text{H}^+)$ cations located on each side of the $[\text{Fe}(\text{CN})_6]^{3-}$ anions, with O-O distances presented in table 4. This precise location of the $(2\text{-}2\text{H}^+)$ cations enables the formation of $\text{O-H}\cdots\text{OH}$ interactions, as shown by the decrease of the O-O distance when x is decreasing (see table 4). As already mentioned, the hydroxyl groups also interact with the

water molecules located inside the cavities of the honeycomb-like structure.

Figure 4: Polyhedral representations of the isomeric pattern for localisation of (1-2H⁺) (as blue losange) and (2-2H⁺) (as violet losange with a partial occupation rate of (2-2H⁺)) in the solid solutions (1-2H⁺)_{3x}(2-2H⁺)_{3(1-x)}[Fe(CN)₆]³⁻² for a) **4** (x= 0.80 and phase A) b) **5** and **6** (x=0.67 and 0.53 phase B) c) **7** (x= 0.37 and phase B) and d) **8** (x= 0.17 and phase C). The green octahedron represents the [Fe(CN)₆]³⁻ anions.

Table 4: Data for the (1-2H⁺)_{3x}(2-2H⁺)_{3(1-x)}[Fe(CN)₆]³⁻² solid solutions (compounds **3-9**): observed phases, isomeric patterns and occupation rates for O in cation (2-2H⁺)

	x	d _{O-O} in (2-2H ⁺) (Å)
[1-2H ⁺] ₃ [Fe(CN) ₆] ³⁻² 3 ²¹	1	-
[(1-2H ⁺) _{0.80} (2-2H ⁺) _{0.20}] ₃ [Fe(CN) ₆] ³⁻² 4	0.80	3.010(5)
[(1-2H ⁺) _{0.67} (2-2H ⁺) _{0.33}] ₃ [Fe(CN) ₆] ³⁻² 5	0.67	2.933 (6)
[(1-2H ⁺) _{0.53} (2-2H ⁺) _{0.47}] ₃ [Fe(CN) ₆] ³⁻² 6	0.53	2.861(4)
[(1-2H ⁺) _{0.37} (2-2H ⁺) _{0.63}] ₃ [Fe(CN) ₆] ³⁻² 7	0.37	2.842(5)
[(1-2H ⁺) _{0.17} (2-2H ⁺) _{0.83}] ₃ [Fe(CN) ₆] ³⁻² 8	0.17	2.834(6)
[2-2H ⁺] ₃ [Fe(CN) ₆] ³⁻² 9 ²¹	0	2.828(5)

XRPD diagrams

For compounds **4-8**, the phase purity was confirmed by X-ray powder diffraction. XRPD diagrams of compounds crystallising in phase **A** (**3** and **4**) are displayed in figure 5, the diagrams for compounds crystallising in phase **B** (**5-7**) are displayed in figure 6 and the ones crystallising in phase **C** (**8** and **9**) are presented in figure 7. This is another proof for the obtention of one pure polycrystalline phase for each defined x value in the solid solutions of formula (1-2H⁺)_{3x}(2-2H⁺)_{3(1-x)}[Fe(CN)₆]³⁻² .n H₂O.

Figure 5: Experimental XRPD patterns for (1-2H⁺)_{3x}(2-2H⁺)_{3(1-x)}[Fe(CN)₆]³⁻² . nH₂O solid solutions crystallising in phase **A**, **3** (b) and **4** (x=0.80) (c), compared to the diagram simulated for **3** (a).

Figure 6: Experimental XRPD patterns for (1-2H⁺)_{3x}(2-2H⁺)_{3(1-x)}[Fe(CN)₆]³⁻² . nH₂O solid solutions crystallising in phase **B**, **5** (x=0.67) (b), **6** (x=0.53) (c) and **7** (x=0.37) (d) compared to the diagram simulated for **6** (a).

Figure 7: Experimental XRPD patterns for $(1-2H^+)_{3x}(2-2H^+)_{3(1-x)}([Fe(CN)_6]^{3-})_2 \cdot nH_2O$ solid solutions crystallising in phase **C**, **8** ($x=0.17$) (b) and **9** (c), compared to the diagram simulated for **9** (a).

Thermal properties

The thermal properties of the formed solid-solutions were investigated using TGA measurements, as already shown in the pure $(1-2H^+)_3([Fe(CN)_6]_2 \cdot 7H_2O)$ and $(2-2H^+)_3([Fe(CN)_6]_2 \cdot 8H_2O)$ phases that exhibit respectively water release temperatures of 100 and 150 °C.²¹

Figure 8: TGA curves (heat of rate 10 °C/mn) obtained for compounds of general formula $(1-2H^+)_{3x}(2-2H^+)_{3(1-x)}([Fe(CN)_6]^{3-})_2 \cdot nH_2O$ **3** ($x=1$) (black), **4** ($x=0.80$) (blue), **5** ($x=0.67$) (dark green), **6** ($x=0.53$) (light green), **7** ($x=0.37$) (red), **8** ($x=0.17$) (orange) and **9** ($x=0$) (dashed black).

The TGA traces (figure 8) confirm the water molecule contents of the polycrystalline samples for **4-8**, varying from 7 to 8, also confirmed by X ray diffraction on single crystals and by EA.

As already shown,²¹ compared to compound **3**, the water molecules in the channels of compound **9** are stabilized by the H-bonding interactions with the OH groups in **2-2H⁺**, resulting in the higher dehydration temperature for *ca.* 50 °C.

Thus, for the $(1-2H^+)_{3x}(2-2H^+)_{3(1-x)}([Fe(CN)_6]^{3-})_2 \cdot nH_2O$ solid solutions, the water release temperature increases when x decreases because of the increasing hydrophilic nature of the channels generated with **2-2H⁺**: at 10 °C/mn heating rate, it varies between 100 °C ($(1-2H^+)_3([Fe(CN)_6]^{3-})_2$) and 150 °C ($(2-2H^+)_3([Fe(CN)_6]^{3-})_2$).

However, the temperature of water release is not linear with the x value.

The temperature of water release is low (around 100 °C) for compounds with high x values (**3**, **4** and **5**). With lower x values, the release temperature increases rapidly to 130 °C (**6**) and 140 °C (**7** and **8**): this is in accordance with the fact that there is no preferential localization of the cations at the

periphery of the channels, and that there is a statistic distribution of the **(2-2H⁺)** cations in the formed structure in **7** and **8**, as shown in figure 4d.

Conclusions

A new family of inorganic-organic hybrid non-isostructural solid solution has been synthesised and crystallized: $(1-2H^+)_{3x}(2-2H^+)_{3(1-x)}([Fe(CN)_6]^{3-})_2 \cdot nH_2O$, by changing the ratio of H-bond donors **Y-2H⁺** (**Y**=1 or 2, $0 < x < 1$ and $n=7$ or 8). Their structure has been carefully analysed and refined. The predictable compositions are confirmed by the single crystal XRD and TGA analysis. We were able to show that finely tuning of the x value allowed us to evidences three different crystallographic phases, which corresponds to three different pavages of the (6,3) network for solid state solutions, and only one preferential localization of the organic cations within the structure. The simplified structural phase diagram can be derived from these data, as shown in figure 9.

Figure 9: Simplified structural phase diagram for solid solutions of general formula $(1-2H^+)_{3x}(2-2H^+)_{3(1-x)}([Fe(CN)_6]^{3-})_2 \cdot nH_2O$, depending on the x values.

The driving force for this observation is the formation of hydrogen bonds between adjacent **(2-2H⁺)** cations within the network. The control of porous properties in solid solution is also explained to the light of the localization of the cations in the network.

Experimental section

FT-IR spectra were recorded on a Perkin Elmer ATR spectrometer.

Microanalyses were performed by the Service de Microanalyses de la Fédération de Recherche Chimie, Université de Strasbourg, Strasbourg, France.

Bisamidinium dications **(1-2H⁺)**^{13a,b} and **(2-2H⁺)**²¹ have been prepared as described in the corresponding literature. Compounds **3** and **9** have been prepared as reported in the literature.²¹

General method of synthesis for 4-8

The solution of bisamidinium dications (**1-2H⁺**) / (**2-2H⁺**) in EtOH/H₂O (1 mL / 1 mL) was carefully layered on top of a H₂O (2 mL) solution of K₃[Fe(CN)₆] (1.7 mg, 5*10⁻³ mmol) in a test tube. After *ca.* three week at room temperature, light green single crystals appeared in the tube.

Synthesis of compound 4

The following (**1-2H⁺**) / (**2-2H⁺**) ratio was used: 2.5 mg / 0.5 mg, (6.5*10⁻³ mmol / 1.3*10⁻³ mmol). Yield: 69%.

Elemental analysis: calc. (%) for ([C₁₄H₂₀N₄]_{0.80}[C₁₄H₂₀N₄O₂]_{0.20})₃[Fe^{III}(CN)₆]³⁻². 6.8 H₂O: C =49.94; H =5.71; N =25.89. Found: C = 49.92; H = 5.49; N = 25.69. IR data (ν_{C=N}, cm⁻¹): 2114.6.

Synthesis of compound 5

The following (**1-2H⁺**) / (**2-2H⁺**) ratio was used: 2.0 mg / 1.0 mg, (5.2*10⁻³ mmol / 2.6*10⁻³ mmol). Yield: 65%.

Elemental analysis: calc. (%) for ([C₁₄H₂₀N₄]_{0.53}[C₁₄H₂₀N₄O₂]_{0.47})₃[Fe(CN)₆]³⁻². 7.4 H₂O : C =48.57; H =5.65; N =25.17. Found: C = 48.56; H = 5.47; N = 25.10. IR data (ν_{C=N}, cm⁻¹): 2114.5.

Synthesis of compound 6

The following (**1-2H⁺**) / (**2-2H⁺**) ratio was used: 1.5 mg / 1.5 mg, (3.9*10⁻³ mmol / 3.9*10⁻³ mmol). Yield: 72%.

Elemental analysis: calc. (%) for ([C₁₄H₂₀N₄]_{0.67}[C₁₄H₂₀N₄O₂]_{0.33})₃[Fe(CN)₆]³⁻². 7.2 H₂O: C =49.20; H =5.69; N =25.50. Found: C = 49.20; H = 5.54; N = 25.41. IR data (ν_{C=N}, cm⁻¹): 2115.1.

Synthesis of compound 7

The following (**1-2H⁺**) / (**2-2H⁺**) ratio was used: 1.0 mg / 2.0 mg, (2.6*10⁻³ mmol / 5.2*10⁻³ mmol). Yield: 67%.

Elemental analysis: calc. (%) for ([C₁₄H₂₀N₄]_{0.37}[C₁₄H₂₀N₄O₂]_{0.63})₃[Fe(CN)₆]³⁻². 7.5 H₂O: C =47.95; H =5.59; N =24.85. Found: C = 47.95; H = 5.44; N = 24.47. IR data (ν_{C=N}, cm⁻¹): 2115.8.

Synthesis of compound 8 (**1-2H⁺**)_{3x}(**2-2H⁺**)_{3(1-x)}[(Fe(CN)₆]³⁻²) (x = 0.37, 0.53, 0.67 and 0.80)

The following (**1-2H⁺**) / (**2-2H⁺**) ratio was used: 0.5 mg / 2.5mg, (1.3*10⁻³ mmol / 6.5*10⁻³ mmol). Yield: 70%.

Elemental analysis: calc. (%) for ([C₁₄H₂₀N₄]_{0.17}[C₁₄H₂₀N₄O₂]_{0.83})₃[Fe(CN)₆]³⁻². 7.1 H₂O: C = 47.53; H = 5.48; N = 24.64. Found: C = 47.55; H = 5.31; N = 24.43. IR data (ν_{C=N}, cm⁻¹): 2114.3.

Structural studies

Single-Crystal Studies

Data were collected at 173(2) K on a Bruker Apex-II-CCD Diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using graphite-monochromated Mo-Kα (λ= 0.71073 Å) radiation. For all structures, diffraction data were corrected for absorption. Structures were solved using SHELXS-97 and refined by full matrix least-squares on F² using SHELXL-97. The hydrogen atoms were introduced at calculated positions and refined using a riding model.²⁴ In all cases, relative oxygen occupancies were refined around each (**2-2H⁺**) cation. Structures can be obtained free of charge from the Cambridge

Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.
CCDC: 1550164-1550168.

Powder diffraction studies (PXRD)

Diagrams were collected on a Bruker D8 diffractometer using monochromatic Cu-K α radiation with a scanning range between 4 and 40° using a scan step size of 8°/mn.

Thermogravimetric (TGA) Studies

TGA measurements have been performed on Pyris TGA4000 Lab System (Perkin-Elmer), using a N₂ flow of 20 ml/mn and a heat rate of 10°C/ mn

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Table 3: Crystallographic data for structural analyses of (1-2H⁺)_{3x}(2-2H⁺)_{3(1-x)}}[(Fe(CN)₆)₂] (0 < x < 1) **4-8**, together with those of the already reported compounds **3** and **9**.²¹

Phases	A		B			C	
	3 ²¹	4	5	6	7	8	9 ²¹
Composition x	1	0.80	0.67	0.53	0.37	0.17	0
Formula	[1-2H ⁺] ₃ [Fe ^{III} (CN) ₆] ₂ · 7 H ₂ O	[(1-2H ⁺) _{0.80} (2-2H ⁺) _{0.20}] ₃ [Fe ^{III} (CN) ₆] ₂ · 7 H ₂ O	[(1-2H ⁺) _{0.67} (2-2H ⁺) _{0.33}] ₃ [Fe ^{III} (CN) ₆] ₂ · 8 H ₂ O	[(1-2H ⁺) _{0.53} (2-2H ⁺) _{0.47}] ₃ [Fe ^{III} (CN) ₆] ₂ · 8 H ₂ O	[(1-2H ⁺) _{0.37} (2-2H ⁺) _{0.63}] ₃ [Fe ^{III} (CN) ₆] ₂ · 8 H ₂ O	[(1-2H ⁺) _{0.17} (2-2H ⁺) _{0.83}] ₃ [Fe ^{III} (CN) ₆] ₂ · 8 H ₂ O	[2-2H ⁺] ₃ [Fe ^{III} (CN) ₆] ₂ · 8 H ₂ O
Molecular weight	1283.07	1299.07	1333.08	1345.88	1361.89	1381.08	1397.09
Crystal System	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	P $\bar{1}$	P $\bar{1}$	P2 ₁ /n	P2 ₁ /n	P2 ₁ /n	P2 ₁ /n	P2 ₁ /n
a (Å)	7.0949(3)	7.0769(8)	7.0846(5)	7.06960(10)	7.08870(10)	7.1019(3)	7.0978(5)
b (Å)	12.3765(5)	12.5517(14)	35.531(2)	35.4378(7)	35.4699(7)	22.0731(10)	22.2254(16)
c (Å)	17.9534(7)	17.9244(18)	12.6872(8)	12.7602(3)	12.8214(2)	20.6168(10)	20.6357(12)
α (°)	83.580(2)	82.908(5)	90	90	90	90	90
β (°)	87.6101(10)	87.892(5)	94.818(2)	94.7890(10)	94.7200(10)	92.0750(10)	92.363(3)
γ (°)	83.9340(10)	84.717(5)	90	90	90	90	90
V (Å ³)	1557.12(11)	1572.8(3)	3182.4(4)	3185.67(11)	3212.82(9)	3229.8(3)	3252.5(4)
Z	1	1	4	4	4	2	2
Colour	Light green	Light green	Light green	Light green	Light green	Light green	Light green
Crystal dim (mm ³)	0.1x0.06x0.05	0.04x0.04x0.05	0.05x0.05x0.06	0.04x0.04x0.05	0.05x0.06x0.06	0.04x0.05x0.05	0.05x0.04x0.02
D (g/cm ³)	1.368	1.372	1.391	1.395	1.411	1.420	1.428
F(000)	674	682	1400	1396	1432	1448	1304
μ (mm ⁻¹)	0.536	0.533	0.531	0.531	0.530	0.529	0.527
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Number of data meas.	22955	17456	16842	35778	33286	21745	13916
Number of data with I > 2σ(I)	9536	7323 [R(int) = 0.0682]	5524 [R(int) = 0.0347]	8993 [R(int) = 0.0297]	9245 [R(int) = 0.0302]	5689 [R(int) = 0.0290]	6294
R	R1 = 0.0588, wR2 = 0.0814	R1 = 0.0864, wR2 = 0.2133	R1 = 0.0469, wR2 = 0.1135	R1 = 0.0530, wR2 = 0.1381	R1 = 0.0485, wR2 = 0.1179	R1 = 0.0546, wR2 = 0.1362	R1 = 0.1084, wR2 = 0.3045
Rw	R1 = 0.1540, wR2 = 0.1728	R1 = 0.1227, wR2 = 0.2351	R1 = 0.0554, wR2 = 0.1191	R1 = 0.0625, wR2 = 0.1443	R1 = 0.0595, wR2 = 0.1237	R1 = 0.0599, wR2 = 0.1404	R1 = 0.2008, wR2 = 0.2797
GOF	1.087	1.005	1.045	1.022	1.078	1.038	1.055
Largest peak in final difference (eÅ ⁻³)	0.789 and -0.468	1.426 and -0.551	0.722 and -0.445	0.883 and -0.468	0.736 and -0.446	1.383 and -1.390	0.476 and -0.806

$$^a R = \sum (|F_o| - |F_c|) / \sum |F_o|; ^b wR = [\sum (w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2]^{1/2}.$$

Graphical Abstract